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DECONTAMINATION OF LOW-LEVEL LIQUID WASTE AT OAK RIDGE NATIONAL LABORATORY USING A SCAVENGING-PRECIPITATION, ION EXCHANGE PROCESS*

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DECONTAMINATION OF LOW-LEVEL LIQUID WASTE AT OAK RIDGE NATIONAL LABORATORY USING A SCAVENGING-PRECIPITATION, ION EXCHANGE PROCESS[a]

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ABSTRACT

For five and one-half years, liquid wastes at Oak Ridge National Laboratory (ORNL) which contained low levels of beta and gamma activity have been decontaminated by a scavenging-precipitation ion exchange process (SP-IX). Some of the activity is precipitated with caustic, and the remainder is sorbed on a cation resin, Duolite CS-100. Cesium-137 activity is routinely reduced to 30 Bq/L, and ^{90}Sr to 0.5 Bq/L. Operation of the plant in 1977 cost $4.64 per thousand gallons (~0.1¢/L). The routine flow rate is 375 L/min.

INTRODUCTION

From March 1976 to August 1981, aqueous wastes at ORNL containing low levels of beta and gamma activity were decontaminated by a scavenging-precipitation ion exchange process, termed SP-IX. The original laboratory-scale development of this process was carried out by R. R. Holcomb and J. T. Roberts in 1961-63.[1,2] Further development and refinement of the method were carried out in a pilot-plant demonstration, the results of which have been reported by R. E. Brooksbank et al.[3] Prior to the installation of the SP-IX system, ORNL used a marginally satisfactory lime-soda-clay precipitation process which removed only 80 to 85% of the total activity.

A photograph of the Process Waste Treatment Plant is shown in Fig. 1. Construction of this plant, which was started in August 1974 by the Cousins Construction Company, was completed in October 1975 at a total project cost of $1.3 million. The site of this building and auxiliary facilities is shown on the Locality Map, Fig. 2.

The process wastes that are treated in this plant are primarily streams which contain no radioactivity under normal conditions, but, in the event of an equipment failure or human

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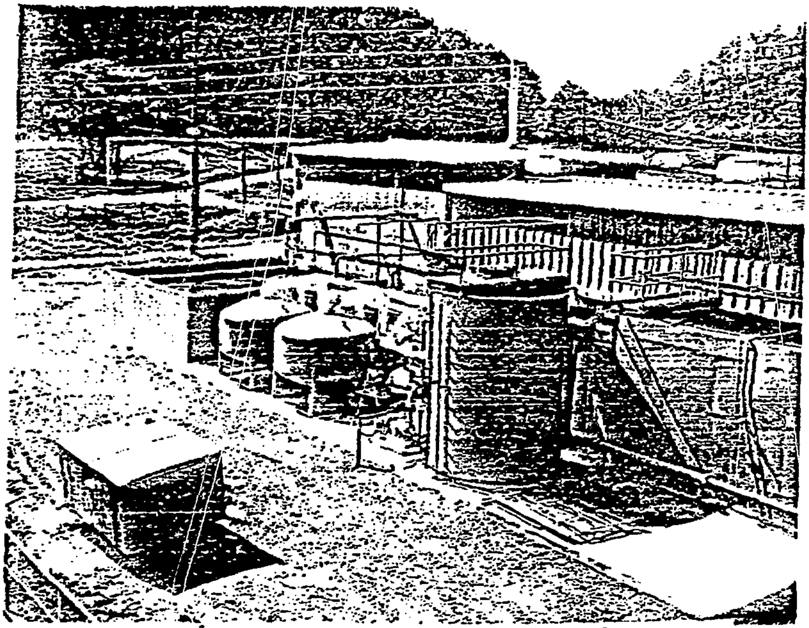
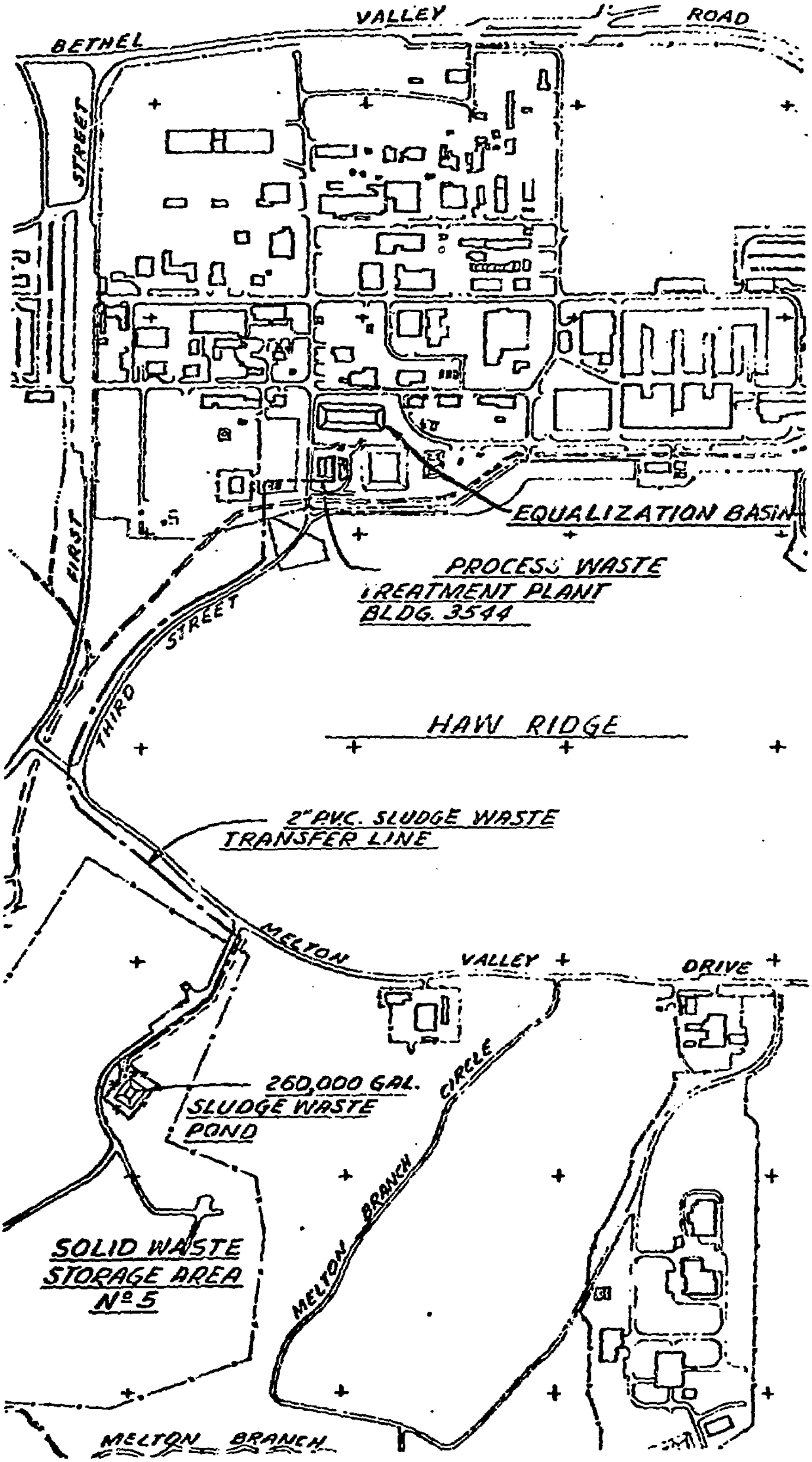


Fig. 1. Process Waste Treatment Plant.

error, could become contaminated. They include such streams as steam condensate from heating coils in vessels containing radioactive solutions, vessel cooling water, rainwater runoff from potentially contaminated areas, condensate from the intermediate-level waste (ILW) evaporator, some building sink and floor drains, etc. The only routine discharge of radioactivity into the waste system comes from the overheads from the ILW evaporator and runoff from certain contaminated areas such as the ILW waste storage tank farm. The average flow rate is ~300 L/min; however, during periods of heavy rainfall, flows >750 L/min sometimes occur. The composition of the process waste varies considerably, but typical analyses are given in Table I.

Table I
Composition of Typical ORNL Low-Level Waste

Constituent	ppm	Constituent	ppm
Total hardness	90-160	Dissolved CO_2	10
Calcium hardness	60-90	Bicarbonate	20-250
Total alkalinity	80-300	Carbonate	0-136
Calcium	20-40	Phosphate	0.11-3.3
Magnesium	2-10	Sulfate	12-34
Sodium	10-35	Fluoride	1-7
Uranium	<0.01	Nitrate	19-142
Copper	0.05	Chloride	5-13
Aluminum	0.01-0.06	Total solids	180-460
Silicon	0-3		
Iron	0.1-0.8	pH	7-10.45
Nickel	0-0.03		
Chromium	0.05		


BETHEL
VALLEY
ROAD
STREET
FIRST
EQUALIZATION BASIN
PROCESS WASTE
TREATMENT PLANT
BLDG. 3544
THIRD
STREET
HAW RIDGE
2" PVC. SLUDGE WASTE
TRANSFER LINE
MELTON
VALLEY
DRIVE
260,000 GAL.
SLUDGE WASTE
POND
MELTON BRANCH CIRCLE
SOLID WASTE
STORAGE AREA
No 5
MELTON BRANCH

Like the other constituents, the radionuclides vary widely in concentration. The activities of special interest are ^{137}Cs and ^{90}Sr, although others (especially ^{60}Co, ^{24}Na, and traces of rare earths) are often present. The range of concentrations found in analyses of feed streams is given in Table II.

Table II
Radionuclide Analyses of ORNL Low-Level Wastes

Constituent	Concentration (Bq/L)
Gross beta	6.7×10^3
^{90}Sr	$9.8 \times 10^2 - 3.7 \times 10^3$
^{137}Cs	$87 - 1.1 \times 10^4$
^{154}Eu	0 - 10
^{60}Co	20 - 412

PROCESS DESCRIPTION

Feed is pumped continuously from the equalization basin and mixed with concentrated sodium hydroxide and a ferrous sulfate solution to give a pH of 11.8 and 5 ppm iron, respectively. These additions take place immediately ahead of a static pipe-mixer. The iron precipitates as a mixture of ferrous and ferric hydroxide, which acts as a scavenger to help flocculate other insoluble materials. The addition of hydroxide is controlled by a downstream electrode, and the addition of ferrous sulfate is controlled by the setting on the feed pump. Coagulation of the precipitate occurs in the flocculator section of the precipitator, where the mixture is gently agitated as it moves, downflow, to the bottom of the clarifier section. Separation is achieved here by upflow of the mixture through a sludge blanket consisting of fluidized particles that trap the floc and continue the precipitation reactions by crystal growth. These particles agglomerate and settle as a slurry in the bottom of the vessel, thus removing ~33% of the activity as well as dirt particles, algae, and most of the hardness from the waste stream. This is similar to the vertical precipitator Model No. 5DS, manufactured by the Permutit Company. The design will handle a flow of 750 L/min.

The sludge is withdrawn periodically and pumped to an agitated 23,000-L holding tank from which it is then removed, as necessary, to a sludge-disposal basin. This consists of a 10^6-L-capacity pit lined with 0.75-mm PVC plastic, located ~1.0 km from the laboratory.

The effluent from the clarifier overflows to a 25,000-L surge tank and is then pumped through one of two pressure-type polishing filters. These two filters, which are used alternately, contain uniformly sized (0.6 to 0.8-mm) anthracite. When the pressure drop through one filter increases significantly, flow is switched to the other, and the first is backwashed to the equalization basin.

The stream from the filter usually contains less than 5 ppm total hardness (as $CaCO_3$). It passes, downflow, through one or two of three ion exchange columns, each containing 1275 L of sodium-form Duolite CS-100 resin. The beds are used consecutively; the use of a bed is discontinued when radiocesium begins to break through (usually after ~2000 bed volumes of feed). The beds are 0.92 m in diameter and 1.84 m high, and the maximum flow rate is held to 380 L/min in each case. However, in periods of high flow into the plant, such as times of heavy rainfall, two beds are loaded simultaneously, in parallel.

Results obtained during the pilot-plant development of this process showed that a movable beta-gamma probe could be used on the exterior of a column to follow a band of maximum activity as the bed was loaded. However, similar probes that were installed on the columns in the plant failed to give meaningful readings; thus, their use was discontinued. This situation was probably caused by the high background readings from ^{24}Na and ^{60}Co. The same difficulty was experienced with a beta-gamma probe located in the effluent stream from the columns. The breakthrough of ^{137}Cs is detected by gamma spectrometry of exit stream samples in an analytical laboratory.

The stream then passes into the first compartment of the clearwell, which is an open, concrete tank with a capacity of 80,000 L. It is divided into two sections by an overflow weir; the first compartment contains two-thirds of the volume. Water from the first compartment is used to backwash the filters and to make up the sodium hydroxide solution used to regenerate the resin columns. The pH is continuously monitored at the weir, and enough sulfuric acid is added to reduce the pH to 7.0. The waste stream then flows into White Oak Creek.

To regenerate a resin bed, it is eluted upflow with two 6375-L (5-bed volume) batches of 0.50 M nitric acid. The first batch removes most of the radioactivity and hardness; it is then concentrated by evaporation, neutralized with sodium hydroxide, and pumped to the ILW disposal system. The second batch is stored and used as the first batch for the next elution. After a water rinse, the resin is reconverted to the sodium form by passing 10 bed volumes of 0.1 M sodium hydroxide upflow through the bed. The caustic and water washes are returned to the equalization basin. The process is shown schematically in the chemical flowsheet, Fig. 3.

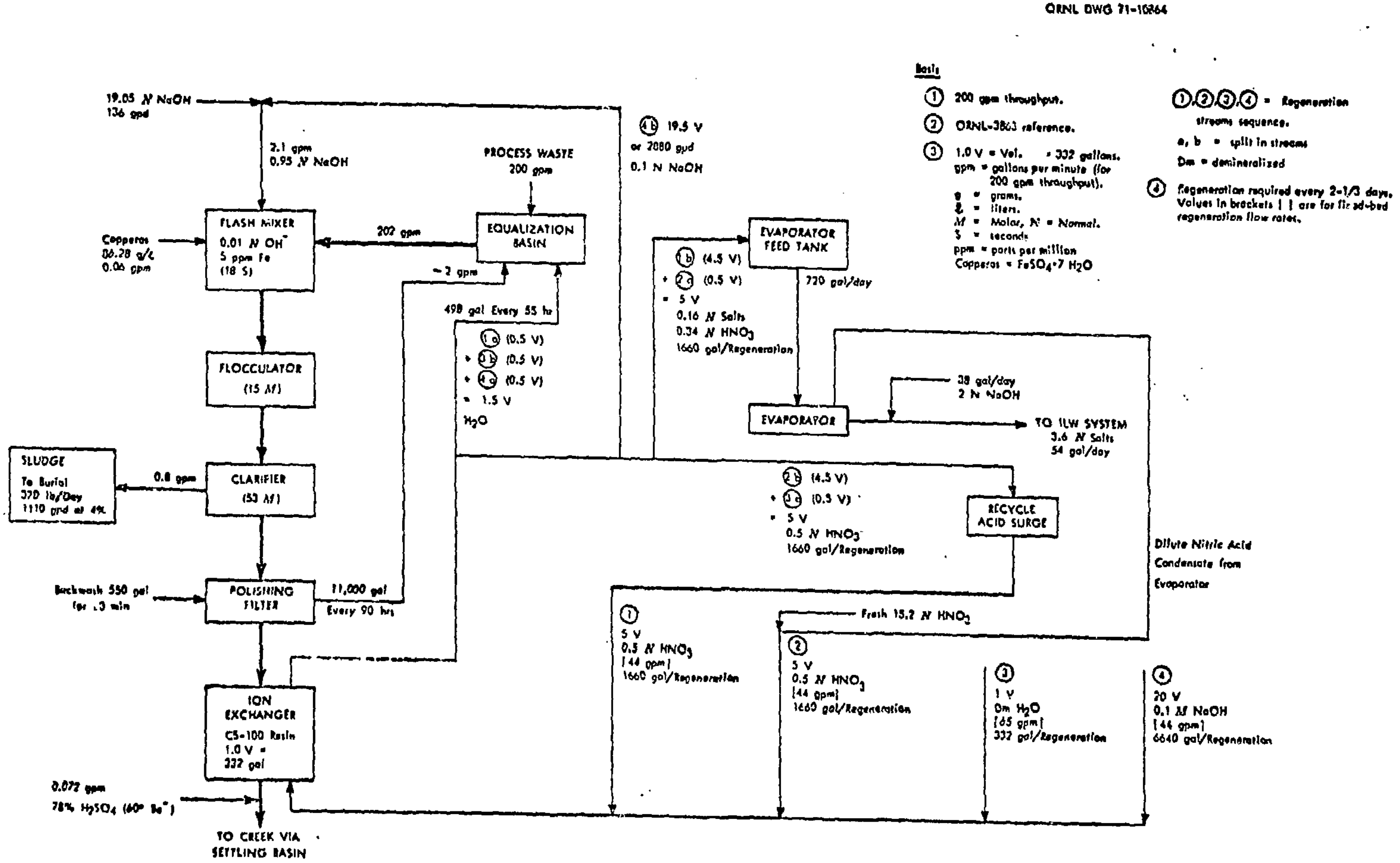


Fig. 3. Process Schematic Chemical Flowsheet.

RESIN CHARACTERISTICS

In February 1978, a detailed study of the total plant operation was carried out by this author.[4] Using actual plant feed from the equalization basin, the lifetime and some of the characteristics of the Duolite CS-100 resin were determined. It was found that the loading capacity for ^{90}Sr is determined by the total capacity of the resin (1.0 eq/L). Since most of the calcium, the predominant multivalent cation present, is removed in the precipitation step, the ^{90}Sr loading is never a problem. However, the loading capacity for ^{137}Cs is determined by its distribution coefficient (DC) on the resin from the feed stream. Although the static DC was found to be ~4000, the DC (vol/vol) from the flowing stream was only ~2000. Hence, the total bed volumes that can be passed before cesium breakthrough is limited to this number. The capacity of the resin decreases slightly through ~20 cycles of loading-elution-regeneration but begins to deteriorate more rapidly with further use. After 30 cycles, the capacity for cesium had been reduced to ~500 bed volumes.

It was also found in this study that the pH of the feed to the resin column must be controlled carefully for most efficient cesium loading. A pH of 11.9 ± 0.1 should be maintained.

COST

The design for this plant was started in 1973 by the ORNL Engineering Division. Site preparation was started in February 1974 by the Rust Engineering Company, and construction of the facility was started in August 1974 by the Cousins Construction Company. Procurement of all major process equipment was carried out by the Union Carbide Corporation—Nuclear Division. Construction was completed in October 1975, at a total project cost of $1.3 million.

Costs for operation of the plant are shown in Table III. These figures are the mean monthly expenses for the early part of 1977. Since the nominal flow through the plant at this time was 3 million gallons per month, the cost averaged $4.64 per thousand gallons (~0.1¢/L) of waste treated.

DECONTAMINATION

The two activities of major concern in the waste process treatment are ^{90}Sr and ^{137}Cs. Other radionuclides, such as ^{24}Na, ^{60}Co, ^{106}Ru, and various rare earths, are also generally present.

The waste treatment process does not remove any of the ^{24}Na that is in the feed. However, the half-life of this radionuclide is so short (15 h) that the total holdup time in the equalization basin, the clarifier, the clearwell, and White Oak Creek is sufficiently long to reduce the activity to an insignificant level.

Table III
Typical Monthly Operating Costs for 1977

	Costs ($/Month)	
Labor		9,894
Operator	5,980	
Maintenance	3,914	
Chemicals		2,161
NaOH ($0.515/gal)	1,133	
HNO_3 (0.30/gal)	72	
H_2SO_4 (1.00/gal)	450	
$FeSO_4$ (0.023/lb)	3	
CS-100 resin (68.65/ft^3)	503	
Utilities		657
Electricity	457	
Steam and water	200	
Analytical services		1,240
Total Cost		13,952

Ruthenium and the rare earths are sometimes present in small, although detectable, amounts. Since these generally exist as trivalent cations, they are precipitated by the hydroxide as well as strongly sorbed by the ion exchange resin. No detectable quantity is found in the plant effluent.

The ^{60}Co is not completely removed by the process. The amount in the feed varies widely (Table II), and laboratory investigations have shown that the cobalt exists as both a cationic species and an anionic species. The cations are completely removed, but the anion passes through and appears in the exit stream. Analysis of a representative feed sample indicated that about one-third of the cobalt was removed in the precipitation step, and one-third on the cation resin; the remaining one-third could be sorbed on an anion resin as proved in the laboratory test.

Decontamination factors (DFs) for the Waste Treatment Plant are somewhat meaningless since the feed concentrations vary so widely, while the activity level in the exit stream remains relatively constant. The activity levels of ^{137}Cs, ^{90}Sr, and ^{60}Co in typical plant effluent and the maximum permissible concentrations allowed in public streams (MPC_W) are shown in Table IV. These levels are reduced when the exit stream is diluted in White Oak Creek, and are still further reduced when White Oak Creek flows into the Clinch River.

Table IV
Radioactivity of Typical Plant Effluent

	In Plant Effluent (Bq/L)	MPC_w (Bq/L)
^{90}Sr	0 - 1.0	11.1
^{137}Cs	0.9 - 52	740
^{60}Co	13 - 46	1850

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